FOOD COMPOSITION AND ADDITIVES

Stoichiometric Determination of Hydroperoxides in Oils by Fourier Transform Near-Infrared Spectroscopy

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A rapid Fourier transform near-infrared (FT-NIR) spectroscopic method was developed for quantitative determination of the peroxide values (PVs) of edible oils. The method is based on the stoichiometric reaction of triphenylphosphine (TPP) with hydroperoxides to produce triphenylphosphine oxide (TPPO). Calibration standards were prepared by adding randomized amounts of TPPO and TPP to peroxide-free high-erucic-acid rapeseed (HEAR) to produce a calibration matrix spanning the concentrations of TPPO and residual TPP in oils having PVs in the range 0–100 after complete reaction of the hydroperoxides with added TPP. A partial-least-squares (PLS) calibration model for predicting PV was developed by using the NIR spectral region from 4710 to 4540 cm^{-1}, where TPP and TPPO both absorb. The resulting PLS calibration was linear, the cross-validation having a standard deviation (SD) of 1.36 PV over the analytical range. The method was validated by comparing the PLS-predicted PVs of oils spiked with *tert*-butyl hydroperoxide (TBHP) and those of naturally oxidized HEAR oils with the results obtained by using the American Oil Chemists' Society (AOCS) iodometric procedure. The FT-NIR PV method correlated very well (SD = 1.20) with the reference AOCS method for TBHP-spiked oil samples. Similar results were obtained for naturally oxidized HEAR oil, with a standard deviation of the difference for reproducibility of ±1.11 PV for both methods. The analysis consists of adding about 0.04 mL TPP stock solution to 1 g oil, shaking, recording the spectrum, and using the PLS calibration to predict PV. Because of its simple and rapid stoichiometric reaction and its excellent correspondence to the iodometric method, the FT-NIR method provides a simple and alternative means of measuring PV. The FT-NIR method avoids the solvent and reagent disposal problems associated with the AOCS method and can be readily automated by appropriate programming of the FTIR spectrometer. Thus, it provides a simple and rapid analytical technique for determining PVs of fats and oils.

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Hydroperoxides formed in lipids by autoxidation are an important quality indicator for edible oils and are useful as a means of assessing the stability of biodegradable lubricants. Their determination is crucial in the edible and industrial fats and oils industry. In the presence of oxygen, lipid autoxidation is initiated by a variety of mechanisms, including heat, light, and metal ions. The reaction leads to formation of hydroperoxides (primary oxidation products), which subsequently break down to produce alcohols and carbonyl compounds (secondary oxidation products) producing the characteristic rancid off flavors (1, 2). Because hydroperoxides are an important indicator of the oxidative status of an oil, American Oil Chemists' Society (AOCS)-approved methods are available for their measurement (3). The key ones are 2 iodometric procedures for determining peroxide value (PV; Cd 8b-90 and Cd 8-53) differing in the solvent used, with chloroform being discontinued because of environmental concerns. Both methods are based on the stoichiometric conversion of KI to molecular iodine by hydroperoxides in an acidic environment and subsequent titration with standardized sodium thiosulfate to determine the amount of molecular iodine released. Although relatively simple, reasonably sensitive, reliable, and reproducible, the iodometric method is labor-intensive and tedious and uses large volumes of acidified solvent, considered environmentally problematic.

A rapid Fourier transform infrared (FTIR) method for quantitative determination of the PV of vegetable oils without the use of reagents was developed previously by our research group. The method is based on use of *tert*-butyl hydroperoxide (TBHP) as calibration standard (4). However, the calibration procedure developed, which used partial-least-squares (PLS) regression to account for potentially interfering factors and components, was too difficult to implement on a routine basis. Because of a substantive study being undertaken in our laboratory on the oxidative stability of biodegradable oil formulations, we were faced with the prospect of performing several thousand PV analyses. This prompted reassessment of our

original approach to PV determination by FTIR spectroscopy and consideration of developing a method that placed less reliance on specialized sample-handling accessories and made use of IR instrumentation more suitable for an industrial setting.

From this standpoint, FT near-infrared (FT-NIR) spectroscopy was considered the instrumental approach of choice, specifically the National Electrical Manufacturers Association-certified Bomem system, which can operate in relatively hostile environments and which has a simple-to-use vial accessory that can use low-cost glass vials with path lengths ranging from 1 to 10 mm. We also wanted the analysis to be independent of oil variability by basing it on a well-defined stoichiometric reaction that could be tracked readily in the NIR region. A detailed mid-IR spectral investigation and chemometric analysis of the reaction of triphenylphosphine (TPP) with hydroperoxides to form triphenylphosphine oxide (TPPO) performed in our laboratory (5) forms the basis of this work. This paper focuses on the development, implementation and performance of an FT-NIR method using the conversion of TPP to TPPO by hydroperoxides to determine the PVs of neat fats and oils.

Experimental

Instrumentation and Sample Handling

The instrument used in this study was a Bomem FT-NIR spectrometer (Hartmann & Braun MB-Series, Bomem, Inc., Quebec) capable of covering the spectral range of 10 000–2000 cm^{-1}, controlled by an IBM-compatible 486 DX-66 MHz PC running under Windows-based Bomem-Grams/386 (Galactic Industries Co., Salem, NH) software. The sample-handling accessory was a temperature-controllable multivial holding block capable of accepting vials of various path lengths. The vials were 8 mm (od) transparent glass (Kimble Glass, Inc., Vineland, NJ) having a volume of ca 1 mL (Figure 1), which were run at 30°C (±1°C). With the cell holder in the IR beam holding a clean empty vial in place, the accessory was aligned to transmit >96% of the incident radiation. For sample analysis, vials were filled with ca 0.7–1.0 mL oil and scanned.

Spectra were recorded by coadding 128 scans at a resolution of 4 cm^{-1}, by using triangular apodization and a gain of 1.0, and their relative contributions were measured against a 128 scan single-beam background spectrum of a clean empty vial. The spectra were subsequently normalized for path length by using a customized normalization routine (Bomem, Inc.), scaling on the peak height at 8262 cm^{-1}, and referenced to 2 baseline points at 9200 and 7600cm^{-1}. The purpose of this procedure was to minimize spectral variations due to variations in vial diameter.

Samples

High-erucic-acid rapeseed (HEAR) oil, used as the base oil for biodegradable oil formulation studies, was provided by Thermal-Lube, Inc. (Montreal, PQ, Canada). The oil was heated at 200°C under vacuum to destroy any hydroperoxides and to remove low-molecular-weight secondary oxidation products. Then it was passed through a column of activated silica gel to remove any remaining partially polar oxygenated molecules. The cleaned HEAR oil was determined to have a PV of <0.50 by the AOCS PV (3) standard method. Reagent-grade TPP (>99%), TPPO (>99%), and TBHP solution (ca

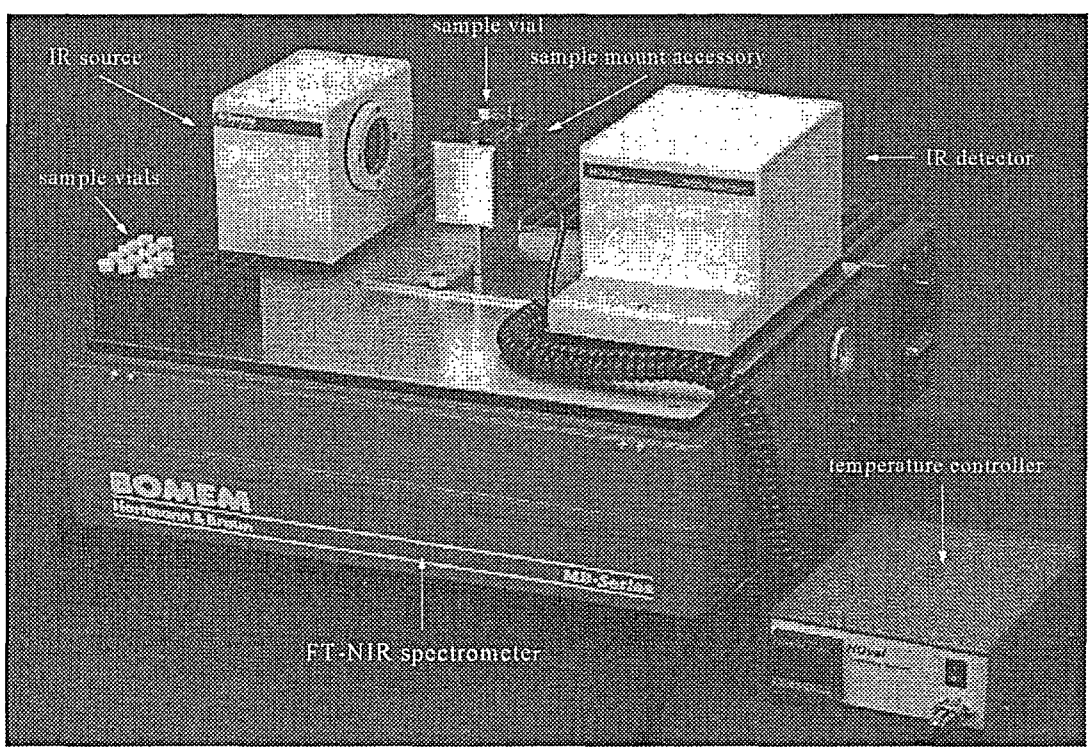

Figure 1. The Bomem MB-series FT-NIR spectrometer with sample mount accessory placed in the IR beam.

5.5M in isooctane; 95% TBHP, 5% H_2O, and 5% butanol) were obtained from Aldrich Chemicals (Milwaukee, WI). Separate concentrated stock solutions (40% w/w) of TPP and TPPO were prepared in chloroform, which was selected as a convenient carrier for uniform dispersion of each reagent in the HEAR oil. The TBHP solution was analyzed by the AOCS method to establish its PV value, and various amounts were added directly to clean HEAR oil as required to obtain oil standards of known hydroperoxide concentration.

Calibration Standards and Calibration and Validation Samples

Calibration standards were prepared by gravimetrically adding known and various amounts (0–1.5 g) of TPPO–chloroform stock solution (40%, w/w) and random amounts (0–1.0 g) of TPP–chloroform stock solution (40%, w/w) into 30 g clean HEAR oil. One gram of each standard was transferred to the 8 mm NIR sample vials and scanned under the instrumental parameters described above, The spectral data were stored to disk for subsequent PLS calibration development. The Nicolet Quant-IR Calibration and Prediction Package (Nicolet Instrument Co., Madison, WI) was used for spectral analysis and PLS calibration (6). Correlation and variance spectra were examined to determine where most of the spectral changes in the calibration set took place. These regions were then explored for calibration development. Each calibration was assessed by using the leave-one-out cross-validation procedure and optimized in terms of the appropriate number of factors by using the predicted residual error sum of squares (PRESS) test. The calibration was considered optimized when the cross-validation error was minimized.

Two sets of validation samples were prepared. One consisted of samples of clean HEAR oil spiked with TBHP, a stable hydroperoxide standard. The other consisted of HEAR oil in which hydroperoxides had been generated by thermal stress. The TBHP validation sample set was prepared by adding various amounts of stock TBHP solution to 30 g clean HEAR to produce samples with PVs ranging from 0 to 100. For the thermally stressed oil set, a high-PV HEAR oil (ca 110 PV) was diluted with clean oil to produce samples covering a range of PVs. Additional time-course validation samples were prepared by heating 200 g HEAR oil at 100°C while oxygen was bubbled continuously through the oil at ca 3 mL/min to accelerate oxidation. Oxidation and sampling were automatically performed by using the continuous oil analysis and treatment (COAT) system (7) devised for monitoring additive levels in oils. The oil was collected automatically at selected time intervals in a fraction collector.

Analytical Protocol

The analytical protocol consisted of transferring ca 1 mL of an oil to an 8 mm NIR vial and adding 0.04 mL 40% stock TPP–chloroform solution with a precalibrated repipette. The amount of TPP added provides a reactant reservoir sufficient to react with the hydroperoxides in samples containing up to an equivalent of 120 PV to produce TPPO. After the TPP reagent has been added, the vial is capped and shaken and is ready for presentation to the FT-NIR spectrometer, where it is scanned. The PV value is subsequently predicted by the PLS TPP/TPPO calibration. All validation samples were also analyzed in parallel by the AOCS PV standard method (3). The results of both methods were compared. All analytical samples were run under the same FTIR operating conditions as the calibration standards.

Results and Discussion

Analytical Concept

In our previous work on developing an FTIR-based PV method, we quantitated hydroperoxides by measuring their characteristic OH stretching absorptions at about 3445 cm^{-1}. This approach was complicated by the large number of potential spectral interferences in this region by other OH-containing species such as alcohols, free fatty acids, moisture, and monoglycerides. A PLS calibration accounting for these interferences was successfully developed, based on the use of calibration standards prepared by adding TBHP and random amounts of potentially interfering compounds to zero-PV oils (4). However, the accuracy and sensitivity of this approach are highly dependent on calibration design, which requires a detailed knowledge of the interfering substances and the magnitude of their influence. Because the compositions of oxidizing oils are rather complex and influenced by various factors, development of this type of calibration is, therefore, not a routine task.

To avoid this complex calibration procedure in the development of an FT-NIR method, we considered the possibility of using a simple stoichiometric reaction as the basis for determining PV. One well-characterized reaction is the stoichiometric conversion of TPP to TPPO in the presence of hydroperoxides. The reaction was described by Nakamura and Maeda (8) in their development of a microassay method for determining lipid hydroperoxide in biological samples by using liquid chromatography with ultraviolet detection. When TPP is in excess, this reaction is rapid and complete, with hydroperoxides being reduced to their respective alcohols and TPP being converted to TPPO according to the following reaction (5):

$$ROOH + X_3{-}P: \rightarrow X_3{-}P{=}O + R{-}OH \qquad [1]$$

where X_3–P: is TPP and X_3–P=O is TPPO.

Studies of the FTIR spectra of TPP and TPPO in the mid-IR region (5) show that the 3 phenyl moieties provide a strong signal and that the binding of oxygen to TPP, forming TPPO, perturbs the phenyl vibrations sufficiently to allow them to be distinguished from those of TPP. Thus TPPO can be quantitated accurately in the presence of TPP through the use of chemometric techniques such as PLS. To investigate the possibility of using the reaction of TPP with hydroperoxides as the basis for an FT-NIR method for PV determination, it was first necessary to evaluate whether TPP and TPPO can be similarly distinguished in the NIR region of the spectrum.

General Spectroscopy

The spectral characteristics of TPP and TPPO in HEAR oil were investigated by adding each component individually to clean HEAR oil, recording the FT-NIR spectrum of the spiked

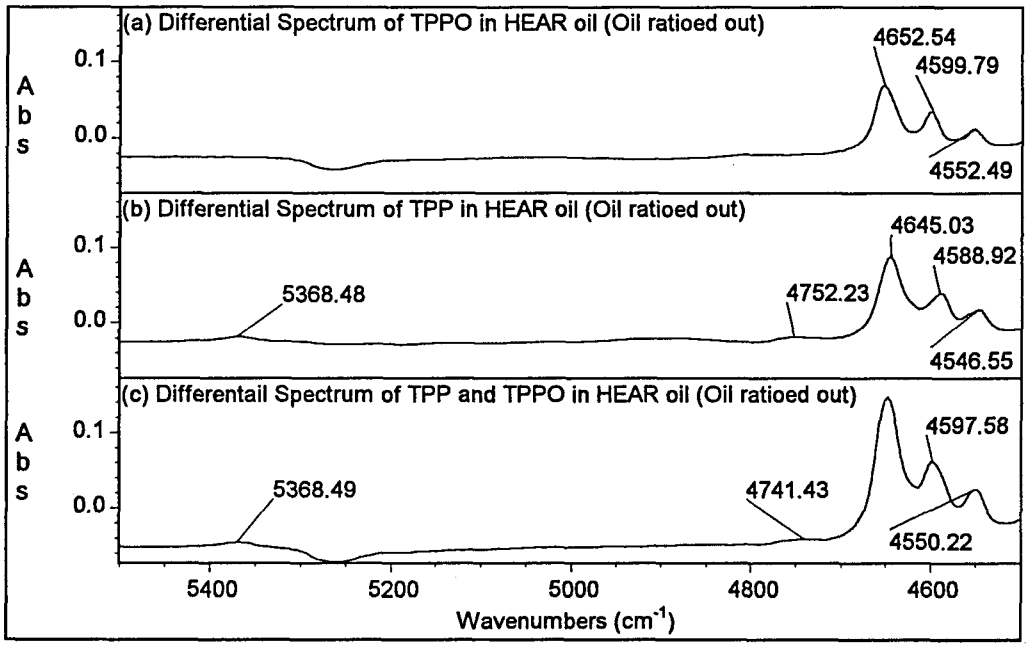

Figure 2. Differential spectra of TPP, TPPO, and a 1:1 TPP–TPPO mixture in HEAR oil after taking out the relative spectral contribution of HEAR oil.

oil, and taking out the relative spectral contribution of the HEAR oil to produce "differential spectra" (9). Figure 2 shows the differential spectra of TPP and TPPO as well as that of a 1:1 mixture of TPP and TPPO over the range 5500–4500 cm^{-1}. TPP gives rise to a series of well-defined bands in the 4714–4500 cm^{-1} region. Although TPPO produces a similar spectral signature, closer inspection shows that the bands are shifted to longer wavelengths. When these 2 compounds are present in a 1:1 ratio, their bands overlap extensively. Under such circumstances, quantitation of individual components generally requires use of chemometric techniques such as PLS to adequately discriminate the relative amounts of each species present.

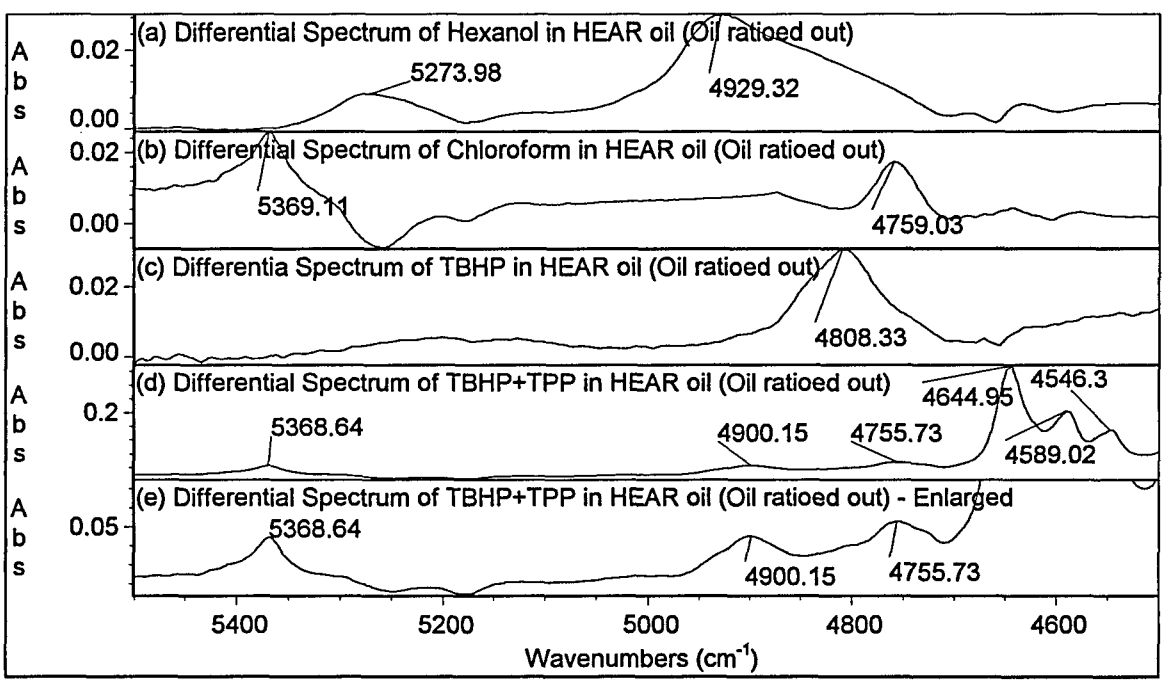

Figure 3. Differential spectra of hexanol, chloroform, TBHP, and TBHP and TPP reacted in HEAR oil after taking out the relative spectral contributions of HEAR oil.

In measuring the amount of TPPO formed in an oil by the reaction of TPP with hydroperoxides present in the oil, the 3 main sources of interference are chloroform (used as a carrier to facilitate dispersion of TPP in the oil), hydroperoxides, and alcohols formed by the reaction. Figure 3 shows spectra of HEAR oil spiked with hexanol, spectrally representative of alcohols that are formed; the solvent chloroform used as a carrier; and TBHP, spectrally representative of lipid hydroperoxides formed in oxidizing oil (4). The absorption bands of these components are well removed from the absorption bands of TPP and TPPO. Figure 3d illustrates the NIR spectrum obtained when TBHP reacts with TPP; this spectrum is magnified in Figure 3e so that weaker bands are more clearly discerned. When Figures 3a–c are compared with Figures 3d and 3e, it is apparent that the TBHP hydroperoxide absorption band at 4808 cm^{-1} (Figure 3c) is lost upon reaction of TBHP with TPP, and a new band appears at about 4900 cm^{-1} (Figures 3d and 3e), which is due to the alcohol formed by the reaction. Thus, the loss of TBHP and the formation of an alcohol are spectrally evident, although the TPP–TPPO spectrum does not visibly appear to be changed. Although measurement of the loss of hydroperoxide, the formation of alcohol, or a combination of both could be a simple basis for determining PV, the complications introduced by hydrogen bonding, the broadness of the hydroperoxide and alcohol bands, and the possible variability of these bands depending on the nature of the hydroperoxide and alcohol (or other OH-containing species) present make this a difficult proposition. A more convenient means of quantitation is to determine the amount of TPPO formed; however, this approach requires that TPPO be accurately measured in the presence of TPP by using a chemometric approach such as PLS. One of the benefits of this approach is that most of the potentially interfering constituents do not absorb in the spectral region of interest. Thus many problems encountered in our previous PV methodology (4) are avoided.

Partial-Least-Squares (PLS) Calibration

Principal-components regression (PCR) and partial-least-squares (PLS) regression are widely used in quantitative NIR analysis as a basis for calibration because the extensive band overlap in the NIR region of the spectrum generally makes it necessary to use statistical techniques to establish correlations between spectral and compositional data. Both calibration approaches are based on compression of spectral data for calibration standards into a set of mathematical "spectra", known as loading spectra. The spectrum of each calibration standard is then decomposed into a weighted sum of the loading spectra, and the weights given to each loading spectrum (known as scores) are regressed against the concentration data for the standards. Because PLS uses concentration data for standards in compression of spectral data, fewer loading spectra are required to account for concentration data than in the PCR approach. This difference makes PLS calibration models potentially more robust. When the PLS calibration model obtained is used to predict unknowns, PLS attempts to reconstruct the spectra of the unknowns from the loading spectra, use the scores (i.e., the amounts of each loading spectrum used in reconstructing the spectrum) for prediction, and use the residual spectra to detect anomalous samples.

Table 1. Calibration matrix for partial-least-squares calibration

Standard No.	PV[a] TPPO	PV[a] TPP
1	0	29.68
2	1.64	79.37
3	2.22	102.36
4	2.49	57.74
5	5.35	11.53
6	9.61	87.46
7	12.04	63.71
8	13.33	40.82
9	19.51	7.11
10	21.37	27.50
11	27.16	63.15
12	32.35	17.73
13	34.75	49.29
14	38.21	33.65
15	47.01	47.55
16	47.23	11.73
17	53.72	24.77
18	58.79	33.86
19	62.75	10.55
20	74.59	22.84
21	78.44	7.56
22	90.82	10.47
23	104.98	2.41

[a] PV = peroxide value; the amounts of TPP (molecular weight = 262.28) and TPPO (molecular weight = 278.29) added to PV-free HEAR oil are expressed in terms of PV units, according to the stoichiometric reaction. An oil containing 1 PV unit of ROOH as determined by the standard iodometric reaction would require 0.1311 g TPP/kg oil, producing 0.1391 g TPPO/kg oil.

Because all the variability in the spectra of calibration standards is accounted for in calibration development, PLS is a very powerful tool for analyzing systems containing multiple components. To develop a robust PLS calibration model, 3 requirements must be met in the design of the calibration standards: (*1*) the concentration range of the component(s) of interest in the samples to be analyzed must be adequately spanned, (*2*) all interfering components that may be present in the samples to be analyzed must be present, and (*3*) there should be no correlation between the concentrations of the interfering components and the component(s) of interest. Thus, in developing a PLS calibration model to predict the amount of TPPO formed in the reaction between TPP and hydroperoxides in the presence of residual TPP, the calibration set must be randomized to avoid building in any correlations between the concentrations of TPP and TPPO, such as would necessarily exist if the standards were prepared by adding a fixed amount of a TPP stock solution to a set of oils covering a range of PVs. To develop a set of appropriate calibration standards, TPPO was added to 30 g samples of clean HEAR oil at concentrations representing

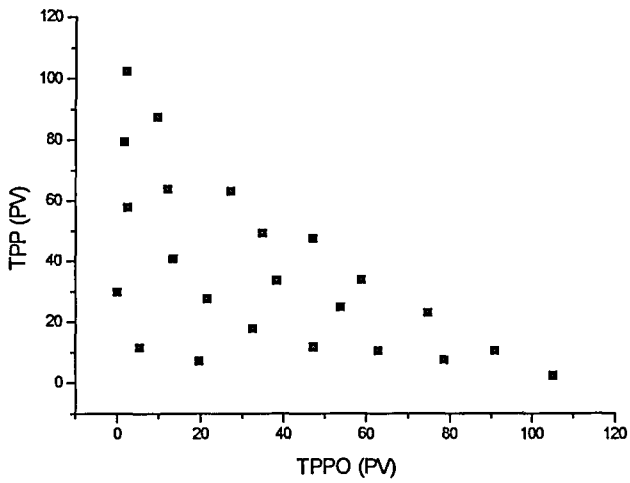

Figure 4. TPP and TPPO composition of PLS calibration standards. The concentrations of TPP and TPPO are expressed in terms of PV units, according to the stoichiometric reaction. An oil containing 1 PV unit of ROOH as determined by the standard iodometric reaction would require 0.1311 g TPP/kg oil, producing 0.1391 g TPPO/kg oil.

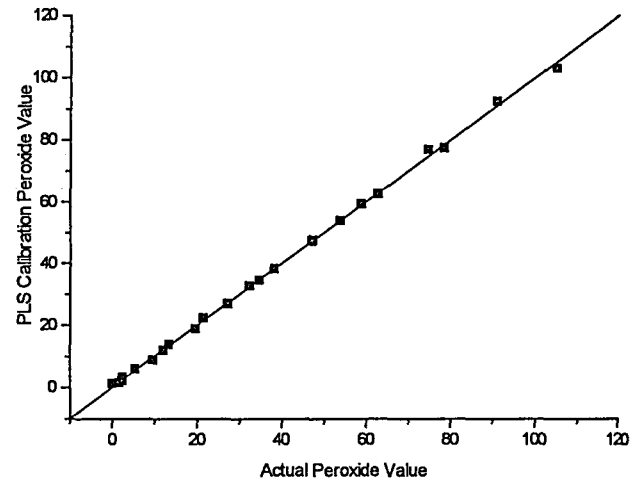

Figure 5. Plot of predicted PV vs the actual PV for 23 calibration standards as derived from the partial-least-squares calibration.

the levels of TPPO that would be produced in oils having PVs in the range 0–105, with TPP subsequently added randomly in amounts representing the various concentrations of residual TPP that might be present at the completion of reaction of TPP with hydroperoxides. Table 1 summarizes the calibration standard matrix used to develop the PLS calibration. Figure 4 shows the matrix in graphical form to better illustrate its randomness and range.

By using this global calibration matrix, a PLS calibration was developed and optimized for the 4710–4540 cm^{-1} spectral region referenced to a single-point baseline at 4710 cm^{-1}. Optimization of wavelength region, baseline selection, and number of factors used in calibration were guided by the PRESS test (6) and minimization of cross-validation error. Figure 5 illustrates the calibration plot obtained from the PLS calibration model based on 4 factors in terms of predicted vs actual PV for the 23 standards. The calibration plot has an overall linear regression SD of 1.00 PV. Using a leave-one-out cross validation procedure, which provides a preliminary estimate of the overall accuracy of the predictions obtained from the calibration, the overall SD was 1.36 PV.

Validation

Figure 6 presents an overlaid plot of duplicate FT-NIR results (SD = 0.633) for serially diluted oxidized HEAR oil samples. Similar reproducibility was obtained for TBHP-spiked samples (SD = 0.875 PV). Figure 7 presents a plot of the means

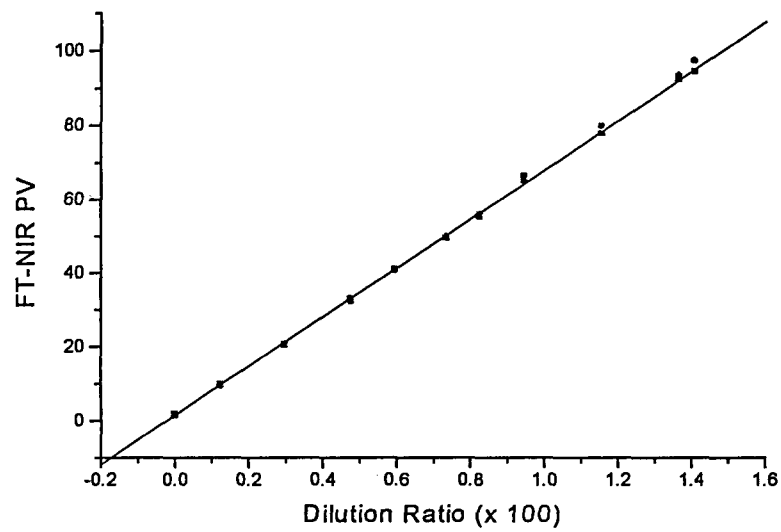

Figure 6. Plot of FT-NIR PV data obtained for a high-PV HEAR oil proportionally diluted with a clean HEAR oil.

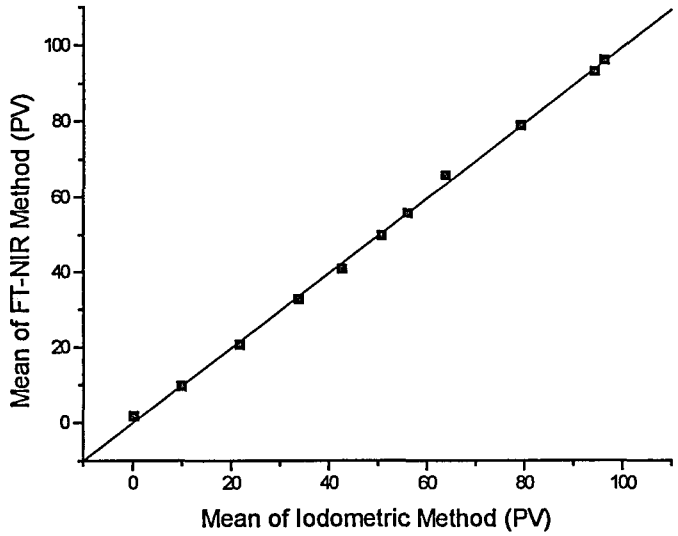

Figure 7. Plot of mean FT-NIR PV values vs. mean iodometric PV values for TBHP-spiked HEAR oils.

of duplicate PV determinations using the iodometric method (IOPV) plotted against the corresponding means of the FT-NIR predictions (FT-NIRPV) for duplicate analyses of TBHP-spiked samples. The plot is highly linear, and the regression equation for the line was

$$\text{FT–NIRPV} = -0.075 + 0.994\,\text{IOPV}, \quad \text{SD} = 1.20,\ r = 0.9994 \qquad [2]$$

The equation indicates that there is a 1:1 correspondence between the FT-NIR predictions and the standard iodometric method. Similar results were obtained for the oxidized HEAR oil dilutions. Further comparisons of the 2 methods in terms of mean differences (MD), standard deviation of the differences (SDD) and coefficient of variation (CV) for reproducibility (r) of duplicate analyses, and the accuracy (a) of the secondary FTIR method relative to the primary iodometric method (9) are summarized in Table 2. There is little to differentiate the performance of the 2 methods, although there is a larger negative bias in terms of accuracy for the oxidized HEAR oil relative to that of the TBHP-spiked samples when compared with the iodometric method. This may be due to the ability of KI to react with both hydroperoxides and peroxides, while TPP may not be as effective in that regard (5). The NIR calibration developed is a general one, designed for performing the active oxygen method (AOM) monitoring of biodegradable oil undergoing thermal stress. As such, it covers a relatively large PV range. In terms of performance, a calibration covering a smaller range, which is more ideal for edible oil analysis, would likely perform somewhat better and be more sensitive if the calibration were devised over a narrower range such as 0–15 PV. Temperature control is desirable, because swings of more than 3°C away from the calibration temperature can affect the reproducibility of results when low PV values are being measured.

Monitoring Oil Oxidation

The McGill IR group is developing a COAT system to monitor oils and additive levels in biodegradable lubricants online (7). In its present configuration, the COAT system is equipped with a mid-IR spectrometer and thus could not be used directly for FT-NIR PV analysis. However, the system was used to perform continuous oxidation and automated sampling of the oil, passing the sample through the spectrometer to a fraction collector. Samples of HEAR oil undergoing thermal stress were collected over time and reacted with TPP and scanned in an FT-NIR spectrometer to simulate the results one might obtain during time-course monitoring of PV, effectively producing an AOM plot. The FT-NIR predictions from the time-course of thermally stressed HEAR oil are compared with results from iodometric analyses of the same samples in Figure 8, again illustrating an excellent concurrence between the 2 methods. Although beyond the scope of this work, these results imply that with appropriate modifications—specifically incorporation of multiple heated oil reservoirs, a common air/oxygen delivery system, control valves, and a dosing mechanism for automatically metering TPP into the oil being sampled—the

Table 2. Mean difference (MD) and standard deviation of the difference (SDD) for reproducibility (r) and accuracy (a) data for PV determinations by FT-NIR and iodometric methods for oxidized and TBHP-spiked HEAR oils

	FT-NIR method		Iodometric method	
Statistic	Thermally stressed HEAR oil	TBHP-spiked HEAR Oil	Thermally stressed HEAR oil	TBHP-spiked HEAR oil
MD_r	±0.543	±0.400	±0.359	±0.007
SDD_r	±1.109	±1.245	±1.118	±0.941
CV_r	1.69%	2.50%	1.71%	1.88%
MD_a	−1.279	−0.381	NA[a]	NA
SDD_a	±1.085	±1.379	NA	NA
CV_a	1.66%	2.76%	NA	NA

[a] NA, not applicable.

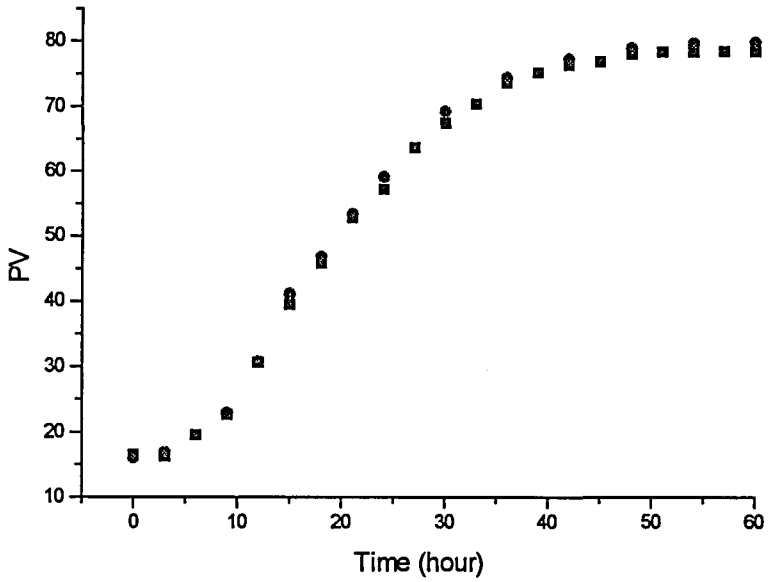

Figure 8. Real-time AOM plot of HEAR oil under forced thermal/oxidation conditions: FT-NIR (■) and iodometric (●) PV results.

COAT system could be used as an automated AOM unit useful for unattended testing of oil stability.

The method developed in this study can be automated readily by programming the FT-NIR spectrometer to perform spectral data collection, processing, and data output presentation. In its simplest form, the PV method entails only adding with a repipette about 0.04 mL TPP–chloroform stock solution to 1 mL oil in an 8 mm glass vial, mixing, scanning, and predicting the PV value by using the PLS calibration. For most applications, the vial-based, at-line approach is simple, rapid, and convenient. For more sophisticated, continuous on-line systems, appropriate modification of the COAT system could provide a means of obtaining true AOM data.

Conclusion

This study demonstrates the overall efficacy of FT-NIR spectroscopy as a means of rapidly and accurately determining PVs of industrial and edible triglyceride-based oils by using the stoichiometric conversion of TPP to TPPO in the presence of hydroperoxides. The FT-NIR method is also a significant improvement over most chemical approaches in terms of avoiding solvent and reagent disposal problems and would reduce labor requirements in routine quality control applications.

Acknowledgments

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